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Paleolimnological Reconstruction of Historical Atmospheric Lead and Mercury Deposition at Lake Tahoe, California−Nevada

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Evidence from this study suggests the existence of a significant modern source for atmospheric Hg deposition in the Sierra Nevada, on the continental west coast of the United States. Concentrations of both lead (Pb) and mercury (Hg) in the sediments of Lake Tahoe deposited prior to 1850 are similar to concentrations in the catchment bedrock, but their concentrations in modern sediments have increased 6-fold for Pb (average 83 ppm) and 5-fold for Hg (average 0.191 ppm). The lake occupies a relatively pristine, nonindustrialized subalpine basin, with a watershed to lake surface ratio of only 1.6. Excess accumulation of trace metals in these sediments should closely reflect direct atmospheric deposition. On average, since 1980 there have been approximately 17 mg of Pb and 38 μg of Hg deposited annually/m^2 in excess of the baseline flux. While Pb emissions occurred locally in the Tahoe Basin, from combustion of leaded gasoline until about 1985, the deposition of atmospheric Hg must represent a predominately regional to global source of contamination. Ratios of total modern flux to preindustrial flux are 29 for Pb and 24 for Hg. The flux ratio for Pb is somewhat higher than reported from the eastern United States and Canada but is not atypical. The flux ratio for Hg is much higher than that observed in most other natural aquatic systems without point-source contamination.

Introduction

Modern industrial processes, product distribution, and material consumption patterns all disperse a wide variety of toxic metals into the environment. Of particular concern is the atmospheric emission of these metals, which can cause significant contamination on a large scale. The introduction of alkyl-leaded gasoline in 1923 ultimately produced a global anthropogenic lead (Pb) emission rate that exceeded the total contribution from natural sources by a factor of 28 (*1*). This airborne Pb contamination was widely dispersed and produced elevated Pb deposition rates around the world, even at remote sites in the Arctic and Antarctic (*2*−*4*). Anthropogenic emission rates fell dramatically, however, as leaded gasoline was phased out of the U.S. market from 1975 through 1995 (*5*); blood lead levels concurrently decreased by nearly 78% in the U.S. population (*6*).

Mercury (Hg) emission rates have also increased in modern times (*7*). It is estimated that global anthropogenic contributions in 1983 were about 1.4 times the natural emissions rate (*1*). The ratio is much less than was determined for Pb. But Hg tends to escape in the elemental form as (Hg^0) vapor, with an average tropospheric residence of about 1 yr (*8*−*10*), whereas Pb emissions from gasoline combustion escaped predominantly as aerosol particulates (*11, 12*), with a mean tropospheric residence of only 6−12 days for the submicron fraction (*12*). This prolonged residence for Hg in the atmosphere may result in significant contamination over extensive areas at the regional to global scale, in a pattern reminiscent of Pb contamination, except that Pb emissions as exhaust particulates were probably constrained to predominately local and regional scales.

Another disturbing characteristic of Hg is biomagnification, whereby even low levels of contamination can produce hazardous concentrations in aquatic based food chains (*13, 14*). Atmospheric deposition and subsequent biomagnification have been associated with elevated concentrations of Hg in fish at numerous sites in Scandinavia, Canada, Florida, and the midwestern United States (*15*−*18*). Sources of contamination in most of these cases were linked to regional industrial processes that produced atmospheric Hg pollution. Long-range transport, however, has also been recognized as a significant component of atmospheric Hg deposition (*10, 19*), and it could assume greater importance as countries around the world continue to industrialize. This global-scale distribution could play a relatively significant role in the western United States, where regional industrial emissions of Hg are comparatively modest (*20, 21*).

To date, there have been few studies of atmospheric deposition of trace metals on the U.S west coast. Those that exist have focused on the urban−industrial centers of Seattle (*22*) and Los Angeles (*23*). Baseline rates and historical deposition patterns have only been reconstructed from sites off the coast of southern California (*24*) and from remote sites in Alaska (*25, 26*). This study therefore looks at the history of atmospheric Hg deposition over a relatively pristine watershed in the Sierra Nevada Mountains of California and Nevada.

Our objective was to compare the modern rates of Hg deposition to preindustrial baseline rates at Lake Tahoe, as reconstructed from sediment cores. There has never been any recorded use of Hg in the Tahoe Basin, but there was substantial Hg production and consumption during the late 1800s in mining districts of California and Nevada adjacent to the Tahoe Basin. We also examine Pb accumulation rates as a useful comparative metric to Hg deposition and compare the results for both Pb and Hg to sediment concentrations and to flux estimates from similar studies in other regions of North America. Concentrations of titanium (Ti), a conservative reference element, were used as correction factors in reconstructing the trace metal deposition rates at Tahoe.

Methods

Study Site. Lake Tahoe occupies a graben in the northern region of the Sierra Nevada Mountains, on the border between California and Nevada (Figure 1). Its surface area is 498 km^2, within a natural basin of 1311 km^2. Less than 8% of the terrestrial area is urbanized (*27*), and growth control limits are now in place. At its natural rim the lake is 1897 m above sea level, but surrounding mountains extend to over 3000 m. On its western boundary, the Tahoe Watershed is delineated by the north-to-south bearing crest of the Sierra Nevada Range.

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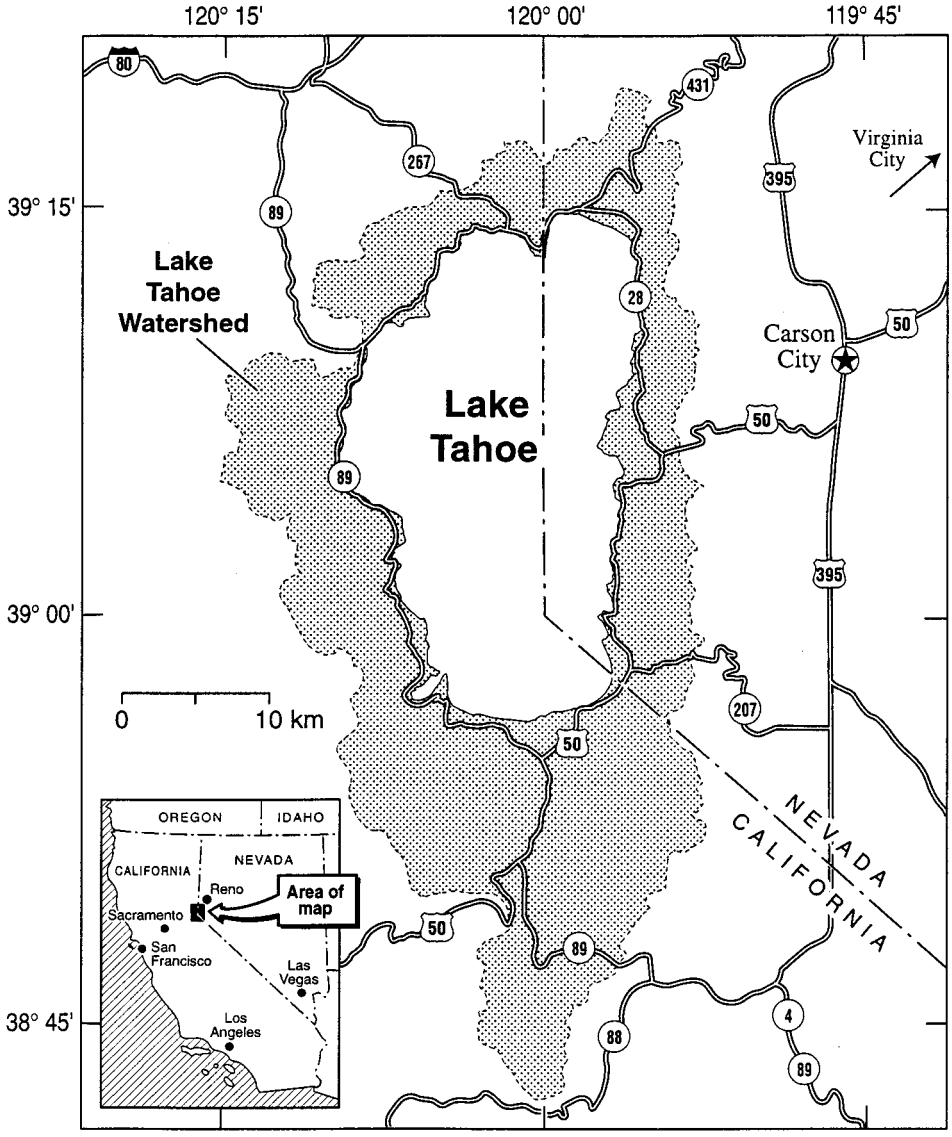

FIGURE 1. Location map of Lake Tahoe and the surrounding areas of California and Nevada. All historical mining areas were outside of the Tahoe Basin, primarily in the western Sierra Foothills between Tahoe and Sacramento and at the Comstock site in Virginia City. Adapted from Rowe and Stone (*34*).

The primary bedrock in the Tahoe Basin is granodiorite, derived from a northern extension of the Sierra Nevada batholith. Extensive andesitic mudflows along the northern boundary of the lake probably contributed to formation of the lake some 2 million years ago (*28*). Since that time, episodic glaciations have scoured most of the basin, so the terrain is quite simple in its composition. Granodiorite dominates all but the northwest quadrant of the basin, which is predominately andesite. Quaternary alluvium, sediments, and glacial deposits cover much of the bedrock at lower elevations, particularly in the south and west areas (*29*).

Beyond urbanized zones most of the basin is heavily forested, primarily with second growth fir and yellow pine. In the late 1800s, this area was extensively logged, and lumber was shipped out of the basin for use as structural timbers in the Comstock Mines of Virginia City, NV. Although this study site is situated between two famous nineteenth century mining districts, the California Mother Lode and the Nevada Comstock, we have found no record of any mineral mining activity in the Lake Tahoe Basin.

Considerable quantities of Hg were consumed during these historic mining periods in the extractive amalgamation of gold and silver from crushed ore. Cinnabar mines discovered in the California coastal range supplied most of this Hg (*30*). It is estimated that up to 12 million kg of Hg was consumed during the California Gold Rush from 1850 to 1900 (*31*). Another 6 million kg was lost during Comstock mining from 1860 to 1900 (*32*). Up to 60% of all this Hg may have been released into the atmosphere (*30*). Substantially elevated Hg concentrations have been found in the biota and sediments of western Sierra streams (*33*).

A bathymetric profile of Lake Tahoe shows a trough-shaped basin, with steep sides and a flat bottom (*34*). Maximum depth is approximately 500 m, with a mean depth of 313 m (Figure 2). The lake is monomictic and ice-free throughout the year. It has one outlet, a hydraulic residence of about 700 yr, and is ultra-oligotrophic (*35*). Because of its extremely low primary productivity, the lake maintains a fully oxygenated water column, with oxidized surface sediments to a depth of about 3 cm. Lake water pH ranges from 7.0 to 8.0, depending upon season and depth.

Sample Collection. The sediment cores examined in this study were extracted with a Soutar box corer, deployed from the University of California—Davis RV *John LeConte*. This device recovers rectangular sections of sediment, approximately 60 cm deep by 30 cm^2, and usually captures the most

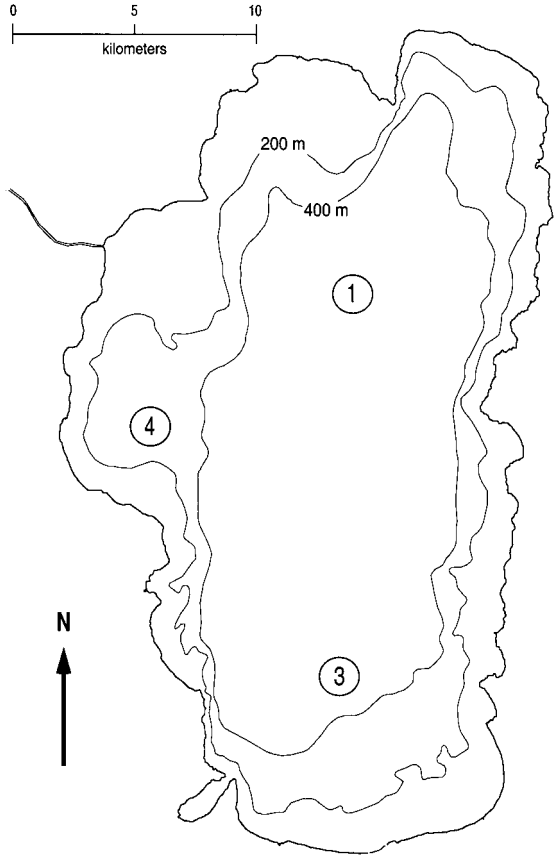

FIGURE 2. Bathymetric profile of Lake Tahoe (modified NOAA map 18665). Sediment sampling locations are indicated for cores (1) LT-91-1, (3) LT-91-3, and (4) LT-91-4. Depth contours are given in meters. Maximum lake depth is about 500 m. Average depth is 313 m.

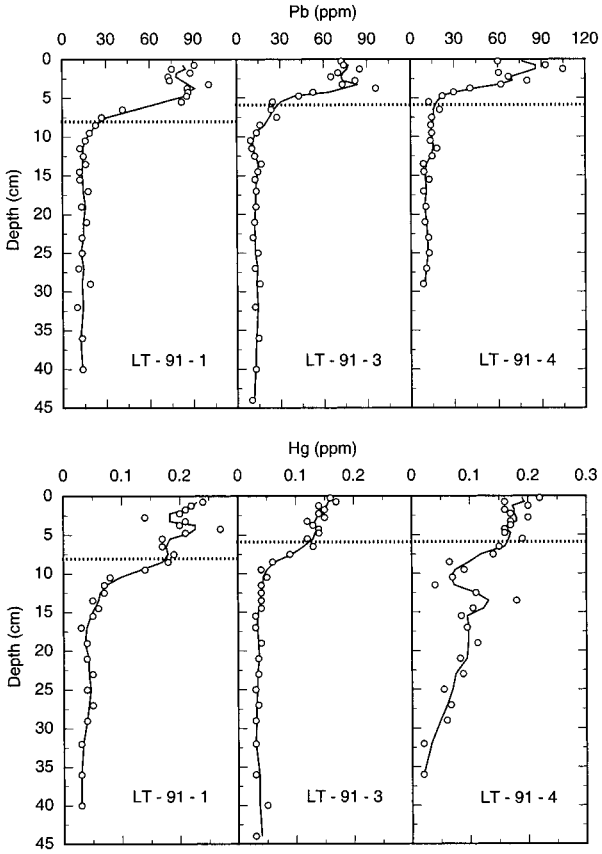

FIGURE 3. Vertical distributions of total Pb and Hg content in three Lake Tahoe sediment cores. The solid line represents a three-term moving average for Pb and Hg concentrations. The dashed line indicates the ^{137}Cs onset horizon in each core, which traditionally corresponds to about 1954.

recently deposited unconsolidated material at the sediment–water interface. Two box cores (LT-91-1 and LT-91-3) were extracted from opposite ends of the lake in the profundal zone below 400 m (Figure 2). A third core (LT-91-4) was taken off the west shoreline on a deep shelf at 300 m depth.

The box core sediments were immediately subcored onboard with 8.9 cm diameter acrylic tubes and then sectioned at regular intervals using a vertical hydraulic extruder. The pattern of sectioning increased with depth, consisting of 0.5-cm intervals from the sediment surface to 5 cm, 1.0-cm intervals to 16 cm, 2-cm intervals to 30 cm, and 4-cm intervals thereafter. There was no evidence of annual varving visible in these sediment cores. Samples were stored at 4 °C in acid-cleaned polypropylene bottles. The results of analyses are represented at midpoint depths for each sediment section.

Analytic Procedures. Concentrations of ^{210}Pb were determined by measuring the activity of its decay product, ^{210}Po, with methods specified in Robbins and Edgington (*36*). The model-specific determination of sedimentation rates for these cores and the assignment of deposition dates were adopted from Robbins (*37*) and from Appleby and Oldfield (*38*). Activity of ^{137}Cs was determined by counting samples for up to 800 min using a low background NaI detector. There was insufficient sample mass to acquire reliable counts from the near surface sections, so the onset horizon of ^{137}Cs was used as an event marker (~1954) in sediment profiles.

The analyses for Pb and Ti were performed by energy-dispersive X-ray spectrometry, with spectra acquired from homogeneous powdered samples on a Kevex 0700 X-ray fluorescence spectrometer. The spectral analysis consisted of ratioing analyte gross peak intensities to Compton and Rayleigh scattered secondary target gross peak intensities. This approach is a nondestructive method of analysis, useful when small amounts of material are available. For Pb we used a zirconium secondary target at 30 kV and 0.31 mA, for Ti we used a germanium target at 20 kV and 0.7 mA. Standard reference materials analyzed under identical conditions gave recoveries within 10% of certified values for Pb and within 20% of certified values for Ti. On average, relative standard deviation (RSD) for multiple sets of sediment sample replicates was less than 20% for Pb and less than 5% for Ti.

Samples for Hg analysis were processed by first digesting in concentrated nitric and sulfuric acids, under pressure, at 80–100 °C for 90 min and then refluxing with potassium permanganate for 90 min. They were subsequently analyzed for total Hg using a modified cold vapor atomic absorption (CVAA) microtechnique (*39, 40*). QA/QC samples passed through all phases of the digest and were treated identically to analytical samples. The level of detection was less than 0.01 ppm. Replication was typically within 5% between samples. Recoveries of certified reference materials were within 20% of certified values. Spike recoveries were within 20% of predicted concentrations. Standard curves demonstrated R^2 values in excess of 0.98.

Results

Pb and Hg Concentration Profiles. The concentrations of Pb and Hg in each sediment section of the three cores from Lake Tahoe are shown in Figure 3 along with the smoothed profiles produced by a three-term moving average. The onset horizon of ^{137}Cs is indicated by a horizontal line at the bottom of the deepest sediment section in which ^{137}Cs was detected. In the absence of significant molecular diffusion or bioturbation, this onset horizon is generally interpreted as rep-

TABLE 1. Concentrations of Pb, Hg, and Ti in Lake Tahoe Sediment Cores with Mean Values, Relative Standard Deviations (RSD), and Sediment Enrichment Factors (SEF) Calculated for each Element

	Pb (ppm)		Hg (ppm)		Ti (wt %)		SEF		
core	surficial	baseline	surficial	baseline	surficial	baseline	Pb	Hg	Ti
LT-91-1	84.7	12.2	0.223	0.030	0.278	0.225	6.0	6.4	0.2
LT-91-3	77.1	12.5	0.157	0.037	0.260	0.259	5.2	3.3	0.0
LT-91-4	85.9	10.5	0.193	0.033	0.306	0.284	7.2	4.8	0.1
mean	82.6	11.7	0.191	0.033	0.281	0.256	6.1	4.9	0.1
RSD (%)	6	9	17	10	8	12	17	32	– –

resenting the first appearance (1952−1954) of global fallout from the atmospheric testing of thermonuclear weapons (*41, 42*). While onset horizons are logically represented at the bottom of sediment sections, the initial fallout could have occurred anywhere within the interval of that sediment section.

Both deep basin cores, LT-91-1 and LT-91-3, show similar patterns in their profiles for Pb and Hg content. The concentrations of these two elements increase dramatically in upper sediment layers, rising over baseline concentrations that are stable and consistent between cores. Although Pb concentrations in core LT-91-4 also demonstrate this pattern, the Hg profile is dissimilar in that concentrations increase transiently over the midcore depths.

In all three cores, Hg concentrations increase substantially prior to the ^{137}Cs onset horizons and prior to equivalent changes in Pb concentrations. Above the ^{137}Cs horizons, however, Hg concentrations increase more slowly. At that point, Pb concentrations begin to increase rapidly, until they stabilize somewhat in the surficial sediments. By contrast, the trend of increasing Hg content persists into these surficial sediments.

It has generally been shown that redox conditions do not appreciably influence the structure of Hg stratigraphy (*19, 26*). Laboratory experiments with mixed sediments incubated for 27 months have demonstrated that Hg remains immobilized in the sediment, despite dramatic changes in redox conditions (*43*). Generally, it appears that sediment Pb is also immobilized (*19, 44−46*). Therefore, we interpret the changes in Tahoe sediment concentrations to represent temporal patterns in Pb and Hg loading rates.

Sediment Enrichment Factors. Baseline concentrations for each core were calculated as the average value of the three deepest sediment sections for which there were data. Surficial concentrations were likewise calculated as the average of the three shallowest sediment sections. Baseline concentrations range from 11 to 13 ppm for Pb and from 0.03 to 0.037 ppm for Hg. Surficial concentrations range from 77 to 86 ppm for Pb and from 0.157 to 0.223 ppm for Hg. The range in these averages between cores was 12% or less for each fraction, excluding the surficial Hg fraction, which varies about 17% between cores (Table 1).

Sediment enrichment factors (SEF) were calculated from these data according to the formula (*47*):

$$\mathrm{SEF} = (C_s - C_b)/C_b$$

where C_s = surface concentration, and C_b = baseline concentration. On average, surficial sediments of Lake Tahoe are enriched 6-fold over the baseline (or background) concentrations of Pb, and they are enriched about 5-fold over baseline concentrations of Hg (Table 1).

Normalization of Sediment Concentrations. The trace metal content of aquatic sediments is derived both from atmospheric deposition and from weathering of bedrock and soil within the watershed. To accurately reconstruct the historical patterns of atmospheric deposition, sediment profiles should be corrected (normalized) for variable contributions from watershed weathering (*45*). Typically, the trace metal profile is simply expressed in ratio to a crustal reference material like aluminum or titanium (*48*). Alternatively, variable inputs from parent terrigenous material can be estimated from depth-equivalent concentrations of the crustal reference material (*49*). Both approaches assume invariant proportional contribution of these elements from their parent material over time and produce an estimate of sediment enrichment due to changing patterns of atmospheric deposition or local pollution. Since there are no point-source inputs of Pb or Hg pollution at Lake Tahoe, atmospheric inputs are the most likely source of excess sediment concentrations.

Accordingly, the excess concentrations for Pb and Hg were determined in Lake Tahoe cores by factoring to variations in sediment titanium, generally considered a conservative lithogenic element in most depositional environments (*50, 51*):

$$C_z' = C_z - \left[\mathrm{Ti}_z\left(\frac{C_b}{\mathrm{Ti}_b}\right)\right]$$

where C_z' = corrected excess element concentration at depth z, C_z = measured element concentration at z, Ti_z = titanium concentration at depth z, Ti_b = baseline titanium concentration, and C_b = equivalent baseline element concentration.

The normalized profiles of Pb and Hg content (Figure 4) are consistent with uncorrected data (Figure 3), which is evidence that deflections in the concentration profiles are due to variation in rates of atmospheric input. Between cores there is a greater variability in the Hg enrichment than is evident with Pb enrichment. This difference is most pronounced in the excess Hg of core LT-91-4 from about 10 to 30 cm. A slight Hg enrichment is also evident in core LT-91-1 from about 20 to 30 cm. The appropriate calculations for excess (atmospheric) flux to lake sediments employ normalized concentrations of trace metal content to correct for variation in the background contribution from weathering and erosional transport of metals within the watershed.

Sedimentation Rates and Sediment Chronology. Sedimentation rates were established with ^{210}Pb and ^{14}C dating. Various methods exist for interpretation of ^{210}Pb data, including the constant rate of supply (CRS), the constant input concentration (CIC), the constant flux with constant sedimentation rate (CFCS) models, and the segmented or stepwise application of the CFCS (SCFCS) model (*37, 38, 52*). Each method has merit and some distinct disadvantage. With the data currently available at Lake Tahoe, it appears that the SCFCS interpretation is appropriate (*37, 52, 53*). Specifically, we know that land-use patterns changed dramatically over distinct time intervals, which is optimal for application of SCFCS. The ^{137}Cs onset horizon is dated correctly with SCFCS data (1955 ± 6) but is dated too early with the CRS data (1937 ± 13). Each method (except CFCS, by definition) indicates a relatively high sedimentation rate just prior to 1900, followed by decreasing rates that persisted until rapid urbanization in the Tahoe Basin during the 1960s and 1970s.

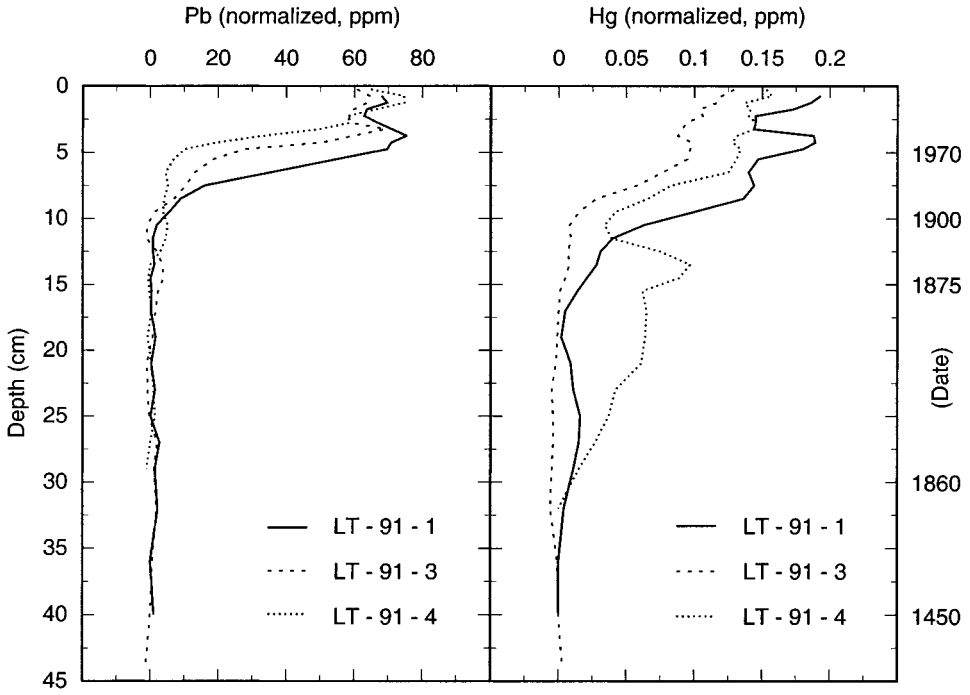

FIGURE 4. Profiles of normalized Pb and Hg concentrations in Lake Tahoe sediment cores, with the data smoothed by a three-term moving average. Approximate deposition dates are shown for reference. The top three dates are derived from SCFCS interpretation of ^{210}Pb data (see text). The 1860 date was located by sediment markers indicating onset of historical logging, and the 1450 date was estimated from ^{14}C data. High mass sedimentation rates occurred during the logging era from 1860 to 1900.

Yet none of these models performed well interpreting data from 1850 to 1900. Under ideal conditions, ^{210}Pb methods have difficulty with that period as the radionuclide decays close to limits of detection. At Lake Tahoe, the sedimentation rates during this period were so high, apparently from the Comstock logging erosion, that residual excess ^{210}Pb has been diluted to near background levels. Independent markers confirm that initial logging impacts (~1860) appear in the sediment record at around 25−30 cm (*53*), well below the profile of excess ^{210}Pb, which ends at 15−20 cm. These markers are evident as coherent changes in biogenic silica and Ti concentrations for each core at that depth (*53*). The CRS method is particularly vulnerable to incomplete profiles and noisy data, with errors propagated to date assignments and sedimentation rates throughout the profile. The SCFCS method does not share this feature, as data are interpreted over independent intervals. Therefore, results for the Tahoe sediments are considered reliable after about 1900.

A pre-disturbance (pre-1850) baseline sedimentation rate was estimated from ^{14}C analysis on several deep consecutive sediment sections below the logging impact markers in two mid-lake cores (*53*). These data produced an average pre-anthropogenic mass sedimentation rate of 0.006 ± 0.003 g cm^{-2} yr^{-1} (95% CI, n = 10). Appropriately, this estimate is somewhat lower than sedimentation rates determined by ^{210}Pb models for the post-Comstock period of watershed recovery in the Tahoe Basin (~1900−1960). The average ^{14}C rate, therefore, is considered a reliable estimate of baseline (pre-disturbance) rates for these lake cores.

All ^{210}Pb dating methods were applied to the data, but for clarity only the SCFCS dates are shown on the profiles (Figure 4). The 1860 date is derived from event markers, as described above. Despite variation in the dates assigned by different ^{210}Pb models, we found that features in the Pb and Hg profiles were dated consistently to within about 1 or 2 decades by each method (*53*). The normalized concentrations for Pb first shifted above baseline after about 1900−1920 and then increased dramatically over the interval from about 1920 to 1980. This corresponds with increasing consumption of leaded gasoline from the time of its introduction in 1923 until EPA regulations in 1973 began to restrict its use (*54*). On a slightly different time-line, Hg concentrations first began to rise above baseline around 1860−1870, then increased markedly until about 1930−1950, after which concentrations continued to increase but at a slower rate.

Because of uncertainties associated with high-resolution dating by ^{210}Pb, particularly in this system, we do not focus on reconstructing time-line profiles for trace metal accumulation. The dates shown in Figure 4 are considered relatively accurate but should not be over-interpreted. Instead, we prefer to focus on the flux ratio as a reliable indicator of change in trace metal accumulation rates over two distinct time intervals. As explained above, the baseline (pre-disturbance) and modern accumulation rates are considered relatively accurate for this purpose.

Hg and Pb Flux at Lake Tahoe. Sediment fluxes of Pb and Hg were calculated as the product of sediment concentration and mass sedimentation rate. Since mass sedimentation rate is the dominant factor in these calculations, a range of flux estimates are possible, depending upon the particular ^{210}Pb model used. Three models were chosen to represent this range (CRS, CFCS, and SCFCS). Although we believe the SCFCS interpretation is appropriate, other models are frequently advocated in the literature, so we have calculated flux with each method to demonstrate that high flux rates and ratios result in any case. Below the range of ^{210}Pb dating and the 1860 event markers, we have used ^{14}C dating to establish an average baseline sedimentation rate for SCFCS and CRS reconstructions. For the CFCS model, a single (constant) ^{210}Pb rate was applied throughout the core profile. In each case, the fluxes were integrated across depth then averaged over the designated time intervals (modern and preindustrial).

These data are summarized for the modern (post-1980) deposition period in Table 2. For modern sediments, with equal weight given to each core, the estimates of excess

TABLE 2. Modern Flux of Excess Pb and Hg to Sediment[a]

	Pb (mg m^{-2} yr^{-1})			Hg (μg m^{-2} yr^{-1})		
core	CFCS	CRS	SCFCS	CFCS	CRS	SCFCS
LT-91-1	11.6	10.5	18.3	31.1	28.1	49.0
LT-91-3	9.2	8.7	13.8	17.1	16.1	25.6
LT-91-4	12.8	12.6	18.3	26.9	26.8	38.6
mean	11	11	17	25	24	38

[a] Flux calculated from normalized concentrations of Pb and Hg. Mass sedimentation rates calculated from three ^{210}Pb interpretations: CFCS (nonlinear constant flux constant sedimentation rate), CRS (constant rate of supply), and SCFCS (stepwise constant flux constant sedimentation rate). The SCFCS data are considered most reliable; CFCS and CRS data are shown for reference.

TABLE 3. Flux Ratios of Modern to Preindustrial Accumulation Rates[a]

	Pb (flux ratio)			Hg (flux ratio)		
core	CFCS	CRS	SCFCS	CFCS	CRS	SCFCS
LT-91-1	7.0	17.5	30.6	7.4	18.7	32.6
LT-91-3	6.2	13.8	22.0	4.3	9.5	15.2
LT-91-4	8.2	23.0	33.4	5.8	16.5	23.7
mean	7	18	29	6	15	24

[a] Preindustrial interval represents sediment deposition prior to 1850, while modern interval represents sediment deposition after 1980. The concentrations of total Pb and Hg were used in calculating these ratios (with modern and baseline concentrations taken from Table 1). SCFCS data are considered most reliable; CFCS and CRS data are shown for reference.

(normalized) Pb flux range between 11 and 17 mg m^{-2} yr^{-1}. Corresponding estimates for excess Hg flux range from 24 to 38 μg m^{-2} yr^{-1}, depending upon choice of ^{210}Pb model.

A concise representation of change in deposition rate over time within a system is given by the flux ratio (*55*). This is simply the modern flux divided by a baseline, or preindustrial (ante 1850) flux. Like SEF factors, however, this flux ratio must be calculated from the total (i.e., uncorrected) concentrations. Accordingly, the total Pb accumulation rate in modern sediments of Lake Tahoe is 13−20 mg m^{-2} yr^{-1} (depending upon sediment dating model); the total Hg accumulation rate is 29−47 μg m^{-2} yr^{-1}. Equivalently, the baseline accumulation rate for total Pb is 0.7−1.9 mg m^{-2} yr^{-1}, and for Hg it is 2.0−5.3 μg m^{-2} yr^{-1}.

One advantage of the flux ratio, unlike SEF factors, is its independence from historical variation in the mass sedimentation rate, assuming that sedimentation rates have been determined accurately. We have calculated Pb and Hg flux ratios in Tahoe sediments from each of the ^{210}Pb models (Table 3). Note that flux ratios calculated from the CFCS interpretation are equivalent to SEF results. These represent the most conservative interpretation—by assuming there have been no changes in mass sedimentation rate over the period of a core profile. At minimum, therefore, without any change in mass sedimentation rate, the flux of Pb has increased 7-fold since 1850, while the Hg flux has increased about 6-fold. With CRS and SCFCS interpretations of sedimentation rate, these flux ratios range from 18 to 29 for Pb and from 15 to 24 for Hg. The higher values in this range are from SCFCS data, which is considered the appropriate interpretation for this system.

Comparison to Other Studies. Flux ratios are independent of most factors that affect Hg concentrations, such as site conditions, sediment focusing, and site-specific differences in absolute rates of atmospheric Hg deposition. Thus, flux ratios provide a unitless measure for the comparison of changes in Hg deposition between sites and geographic regions (*26, 55*).

The data in Tables 4 and 5 were assembled from studies in North America that provided sufficient details for calculating a modern to preindustrial flux ratio or gave this information explicitly (*17, 25, 47, 56−59*). Studies from aquatic systems with direct industrial inputs were excluded from this compilation. The number of sites per study refers to separate aquatic systems, generally lakes, from which sediment cores were extracted. Reservoirs and marine sites were excluded from these calculations. When more than one core was taken from a system, the individual core results were averaged. These site averages yield the range of values within a study. The mean value was determined as the simple average of all sites within the study. Dates are generally approximate and were either taken directly from the citation or estimated from the mass sedimentation rates. For consistency in comparison with other studies, the modern and preindustrial fluxes at Tahoe were calculated from uncorrected (total) sediment concentrations. The SCFCS interpretation of sedimentation rates was used. Fluxes shown in Table 2 are different from Tables 4 and 5 because they represent the accumulation rates calculated from excess (normalized) concentrations.

At 47 μg m^{-2} yr^{-1}, the average modern flux of Hg (uncorrected) to Lake Tahoe sediments is 24 times greater than the baseline flux was prior to 1850 (2.0 μg m^{-2} yr^{-1}). This produces a modern to baseline flux ratio that is substantially higher than observed in the eastern and midwestern United States or in Alaska and Canada (Table 4). However, neither the modern flux nor the preindustrial flux at Lake Tahoe fall outside the range of results found in other studies. Thus, it appears that high flux ratios for Hg in the Tahoe sediments result from a combination of relatively low preindustrial flux and a comparatively high modern flux.

For Pb, the average modern flux (uncorrected) to Lake Tahoe sediments is 20 mg m^{-2} yr^{-1}. The average preindustrial accumulation rate is 0.7 mg m^{-2} yr^{-1}. These values are similar to the Pb accumulation rates found at other sites (Table 5). The flux ratio for Pb at Tahoe is more similar to that found at other sites than are the Hg flux ratios. Notably, the Johnson et al. (*57*) study indicates a flux ratio for Pb in the Midwest that is equivalent to what was found at Tahoe. That is not the case for Hg flux ratios, which differ significantly between these two sites.

Discussion

One of the more interesting findings of this study is that Hg flux on the U.S. continental west coast near the crest of the Sierra Nevada Mountains may be equivalent to or greater than rates of Hg deposition observed in the Midwest and Eastern United States or in Alaska and Canada. General assumptions would suggest that relatively pristine air masses from the Pacific Ocean become incrementally burdened by regional and local sources of air pollution as they move across the continent. This contributes to the high rate of atmospheric Hg deposition found at many sites in the Midwest and on the east coast of the United States and Canada (*7, 21*). It would now appear, however, that air parcels coming off the Pacific could bring substantial atmospheric Hg onto the continent or may entrain significant Hg from regional sources on the west coast. In the context of this study it is difficult to say which process dominates, but several factors can be considered that will provide a better sense of the potential relative contribution from these sources.

Natural rates of Hg emission have been estimated to account for about 40−45% of the total global atmospheric loading (*1, 10, 60*). This yields a ratio of 2.4 for total modern emissions over the natural background rate. Notably, this is comparable to an average flux ratio of about 2.0 that was determined from sediment cores of three pristine coastal lakes in southeast Alaska (*26*); a study that was not included

TABLE 4. Compilation of Total Mercury (THg) Flux to Sediments of Aquatic Freshwater Systems in North America[a]

location	no. of sites	modern interval[b]	modern THg flux (μg m^{-2} yr^{-1})	preindustrial interval[b]	preindustrial THg flux (μg m^{-1} yr^{-1})	sediment enrichment factor	Hg flux ratio (modern vs preindustrial)	ref
S. Florida	5	p. 1985	34−79 (50)	a. 1900	8−14 (11)	0.8−2.7 (1.7)	3.4−8.7 (6.0)	*17*
Lake Tahoe	1	p. 1980	47[c]	a. 1850	2.0[c]	4.9	24	this study
Minnesota−Wisconsin	7	p. 1980	16−32 (23)	a. 1850	4.5−9.0 (6.4)	1.3−3.2 (2.5)	3.2−4.9 (3.7)	*47*
N. Canada	10	c. 1990	4−37 (14.6)	a. 1700	0.7−25.1 (7.4)	0.2−6.0 (1.7)	1.2−7.0 (2.7)	*56*
S. Ontario	5	c. 1980	10−44 (22)	a. 1900	4.8−13.6 (10)	1.6−4.5 (2.4)	1.5−3.2 (2.2)	*57*
N. Alaska	2	p. 1960	1.6−7.5 (4.6)	a. 1845	1.4−6.1 (3.7)	0.2	1.2	*25*

[a] Values for flux are presented as the range and (mean) of all relevant sites in the study, with site value determined as the average of any multiple cores listed. Note that flux values have been rounded, but flux ratios are accurate as listed. Only those sites are represented that do not receive any direct industrial discharge. [b] When dates were not given explicitly in the report, they were estimated from sedimentation rates (a. = ante, c. = cerca, p. = post). [c] For consistency between studies, the Lake Tahoe Hg fluxes presented here were calculated from uncorrected concentrations (Table 1).

TABLE 5. Compilation of Total Lead (TPb) Flux to Sediments of Aquatic Freshwater Systems in North America[a]

location	no. of sites	modern interval[b]	modern TPb flux (mg m^{-2} yr^{-1})	preindustrial interval[b]	preindustria TPb flux (mg m^{-2} yr^{-1})	sediment enrichment factor	Pb flux ratio (modern vs preindustrial)	ref
Adirondack State Park	1	p. 1970	61	a. 1940	5.4	9.5	11	*58*
Lake Tahoe	1	p. 1980	20[c]	a. 1850	0.7[c]	6.1	29	this study
Lake Michigan (S. Basin)	13	c. 1972	15	a. 1900	1.6	8.1	9	*59*
S. Ontario	5	c. 1980	4−11 (9)	a. 1900	0.2−1.3 (0.5)	9−46 (20)	17−28 (22)	*57*
N. Wisconsin	1	c. 1979	12	a. 1800	2	7.6	6	*78*

[a] See footnotes for Table 4.

in Table 4 because the fluxes were not reported. Considering that area remote from anthropogenic sources of Hg emission, with prevailing winds out of the Pacific, the total increase in Hg flux was interpreted as representing globally distributed emissions. This flux ratio would indicate a 2-fold increase since 1850. The authors applied this number as a scaling factor to sediment Hg profiles of several lakes in the Midwestern United States, thereby doubling the reconstructed preindustrial Hg flux and accounting for about 60% of the modern flux. They surmised, thus, that some 40% of total modern Hg flux at these midwestern lakes was derived from regional continental anthropogenic emission sources (*26*).

At Lake Tahoe, a doubling of the entire baseline Hg flux (2.0 μg m^{-2} yr^{-1}) would account for less than 5 μg m^{-2} yr^{-1}, which is only 12% of the excess modern flux (38 μg m^{-2} yr^{-1}). This would suggest, assuming there are no latitudinal differences in globally distributed atmospheric Hg at the hemispheric scale, that more than 85% of modern atmospheric deposition in Lake Tahoe is derived from regional sources. Although latitudinal gradients in globally distributed Hg may exist, there is insufficient evidence to assess their relative importance over these study sites. However, extensive data from Landers et al. (*20*) for boreal and arctic landscapes in Alaska, Canada, Scandinavia, and Russia suggest that such latitudinal stratification is only a minor component of the variation in flux for atmospheric Hg. Instead, regional or supra-regional sources and processes seem to dominate the variation in flux over those areas.

One caveat in the scaling of flux ratios between sites is an inherent sensitivity to differences in the baseline flux of Hg contributed from watershed erosion of parent terrigenous material and natural background atmospheric input (*55*). Generally, these ratios should not be scaled across systems in a comparative sense, unless the estimates of baseline contribution are accurate and equivalent. The baseline (preindustrial) flux of Hg at Tahoe is lower than found in most other systems but is considered accurate since concentrations of Hg in the bedrock materials are about equal to baseline concentrations found in the lake sediment, allowing for some allochthonous dilution (*53*). This suggests that background atmospheric Hg deposition in the Tahoe Basin prior to 1850 was minimal. The high flux ratio, however, indicates a dramatic increase in Hg deposition since that time, although there never been any recorded use of Hg in the Lake Tahoe Basin.

Unlike Hg, there has been a local source of historical Pb emissions at Lake Tahoe, in the form of leaded gasoline consumption. Interestingly, this can provide some validation for the relatively high rate of modern Hg deposition estimated for this site. Atmospheric residence times for Pb particulates are largely a function of their size distributions. Various studies have shown that more than 50% of automotive Pb emissions occur as particulates greater than 1 μm, which tend to accumulate within a short distance (~100 m) of roadways (*12*). The typical atmospheric residence times for Pb particulates in urban areas range from 3 to 26 h (*12*). In a comprehensive mass balance study of automotive Pb emissions within the Los Angeles Basin, it was determined that only 33% of this Pb was ultimately wind-blown out of the basin (*11*). Therefore, it seems that a major portion of automotive Pb emissions were locally constrained, which explains the low rate of Pb deposition measured at one remote site in the Sierra Nevada, about 300 km south of Lake Tahoe. The Pb flux in bulk precipitation there was only 0.9 mg m^{-2} yr^{-1} (*61*), despite near maximal consumption of leaded gasoline in urbanized coastal California during that period.

We have calculated automotive Pb emissions at Lake Tahoe for 1976, using fuel consumption records as estimated by in-basin gasoline sales. A regional survey estimated that 24 738 200 gal of gasoline was sold in the basin that year (*62*). We know the average Pb content in gasoline was about 2.0 g gal^{-1} prior to the introduction of unleaded gasoline in 1975 (*54*). By 1976, unleaded gasoline accounted for roughly 18% of the total gasoline market (*5*). Therefore, it is estimated that Pb in all gasoline consumed averaged about 1.6 g gal^{-1} for 1976. The emission factor for leaded gasoline in these calculations was 0.75, with about 25% of Pb retained in the oil, filters, and exhaust system (*23*). On the basis of these numbers, the estimated emission of Pb from automobiles

driven in the Tahoe Basin during 1976 was about 40 t. If we assume that 33% of this Pb was wind-blown out of the basin [as in the Los Angeles study by Huntzicker et al. (*11*)] and that the remainder was uniformly distributed within the Tahoe watershed (1311 km^2), then areal deposition of Pb from local traffic would have amounted to approximately 20 mg m^{-2} in 1976. This is equivalent to the flux reconstructed from Tahoe sediment cores, where excess Pb accumulation in 1976 (three core average, SCFCS model) was 17 mg m^{-2} yr^{-1} (normalized) or 20 mg m^{-2} yr^{-1} (uncorrected). These calculations suggest that sufficient Pb was emitted locally to account for most of the Pb burden measured in recent sediments of the lake. Furthermore, our baseline flux of Pb to Tahoe sediments (0.7 mg m^{-2} yr^{-1}) is quite similar to Pb deposition measured at the remote Sierran site discussed previously (*61*) and is just slightly greater than a flux of 0.5 mg Pb m^{-2} yr^{-1} measured in bulk precipitation over the eastern central (33−48° N) Pacific Ocean (*63*).

The fact that we can accurately account for Pb burden in the Tahoe sediments, along with its general correspondence to loading rates and flux ratios observed in other studies, suggests that our reconstruction of historical sediment and associated trace metal deposition in this system is reliable. There remain, however, some intriguing contrasts between sediment profiles of Pb and Hg in this system. First, the concentrations of Hg clearly increased prior to Pb concentrations in these sediments. Second, while Pb concentrations have diminished from peaks reached in the 1970s, as would be expected after the introduction of unleaded gasoline, Hg concentrations have continued to increase overall. Third, there is a greater variation in concentrations of Hg between cores than observed for Pb concentrations. Specifically, while the highest concentrations for both elements are observed in the north lake core, the west core shows greater Hg concentrations but lower Pb concentrations than the south lake core. Furthermore, there is a significant increase in the deep core concentration of Hg at that west lake site. All of these features can be explained reasonably by differences in source and delivery patterns for the two elements. It is likely that Hg was brought into the basin by prevailing westerly winds, perhaps with some orographic scavenging as described below, but that Pb has been predominately contributed by automobile emissions distributed around the lake.

While this study represents a first estimate of historical atmospheric Hg deposition for northern California, additional contemporary data comes from a new Mercury Deposition Network (MDN) station located in the coastal range north of San Francisco. The first full year of operation (1998) at this site measured a wet deposition rate for total Hg (THg) of 5.5 μg m^{-2} yr^{-1} (*64*). There are 30 sites in the national network, with most located in the midwest, northeast, and southeast. Total wet deposition of Hg at the California station is about one-half the average rate for all MDN sites (10.5 μg m^{-2}) and has about one-third the volume-weighted average THg concentration in precipitation (9.5 ng L^{-1}). Although dry deposition of Hg was not measured at this site, it is likely to be approximately equivalent to the wet deposition rate (*65*). This would suggest that total (1998) atmospheric Hg fallout in the coastal range of northern California was 11 μg m^{-2}, which is about one-half to one-third the rate of excess THg deposition reconstructed from modern sediments of Lake Tahoe. Therefore, the high rates of Hg deposition at Lake Tahoe must be due to a unique combination of geological, meteorological, and historical factors not usually considered.

In some respects, Lake Tahoe is an ideal site for the paleolimnological reconstruction of historical atmospheric Hg deposition. Its subalpine watershed remains relatively pristine with no industrial emissions that would contribute to local atmospheric Hg loading. The lake's great depth and trough-shaped bathymetry help reduce confounding effects from sediment focusing (*53*), and surface sediments remain oxidized throughout the year. Moreover, direct deposition tends to be most accurately reflected in lakes that have large surface area, relatively small terrestrial catchment, and a long hydraulic residence. Although significant correlation has been demonstrated between Hg flux estimates and the ratio of catchment to lake surface area, Lake Tahoe falls close to the intercept of a linear regression on these factors, which yields a theoretical net deposition rate for lakes with no terrestrial catchment (*47*). In that relationship (for midwestern lakes), a lake-to-catchment ratio of 1.6 (Lake Tahoe) overestimated direct atmospheric Hg deposition by about 40%. Sediment focusing could also enhance Hg deposition estimates at Lake Tahoe, perhaps up to 20%, assuming a complete scavenging of all sediment from the lakebed above 100 m. Taking both factors into consideration would produce an estimate for THg flux in the Tahoe Basin of 28 μg m^{-2} yr^{-1}, a rate that is still significantly greater than flux to the northern California coast and higher than averages from most other studies, except south Florida (Table 4).

The unexpectedly high rate of Hg deposition observed at Tahoe in modern sediments may occur as a result of efficient orographic scavenging by rain and snow. On average, over nonmarine environments, about two-thirds of the total Hg flux is delivered as wet deposition (*10*). Situated at the crest of the Sierra Nevada Range, Lake Tahoe normally receives abundant annual precipitation (15−80 in.) from winter storms that deliver maritime air masses out of the Pacific into northern California and Nevada (*66*). These parcels would be the primary source for globally dispersed tropospheric Hg pollution delivered into the Tahoe Basin. Lower altitude air flowing from the Pacific into the Central Valley through the Coastal Range passage at San Francisco Bay could also entrain regional pollution from San Francisco and Sacramento and then drop much of it in precipitation over the Sierras. Similar orographic scavenger zones have been observed in other highland locations (*67*), and there is independent evidence for transport of atmospheric pollution into the Tahoe Basin from urban and agricultural areas west of the Sierras (*68, 69*).

Another related factor that could significantly enhance Hg deposition over the Tahoe area is the process of cold-condensation—whereby temperature-dependent partitioning and transport increase the concentrations of semivolatile compounds over cooler environments (*70*). Recently, Blais et al. (*71*) found that concentrations of organochlorines increased with altitude over the Canadian Rocky Mountains. To explain this phenomena they suggested a form of cold condensation, where increasing altitude essentially distills semivolatile compounds from the atmosphere. As volatility tends to decrease with temperature, the progressive volatilization from relatively warm areas at lower elevations and a subsequent condensation from adiabatic cooling with increasing altitude causes higher concentrations and accumulation rates over the higher elevations. They found that snowpack inventories of organochlorines increased sharply beyond 2000 m (asl), presumably due to cold condensation and increased precipitation. The cold condensation of Hg has also been demonstrated in a preliminary model by Mackay et al. (*72*). This mechanism, along with orographic precipitation and scavenging could dramatically increase rates of Hg accumulation over high altitude environments like Lake Tahoe, especially when there are regional downwind sources of Hg in a warmer climate at lower elevations.

High temperature combustion processes are the dominant contemporary anthropogenic emission source for Hg, mainly from coal burning and municipal/medical waste incineration (*7, 21, 73*). Modern coal-fired electric power generation plants, for example, lose more than 55% of their feed coal Hg content to the atmosphere (*74*), mostly as Hg vapor. Prior to

implementation of advanced emission control technologies these loss rates were nearly 100%. Neither California nor Nevada have many coal-fired utilities. In fact, the coal consumption in these two states accounted for only 1% of total U.S. consumption in 1990 (*75*). Several other categories of Hg emissions may be considered important under some circumstances, including oil combustion, chlor-alkalai production, smelting of ore and metals, cement production, wood combustion, crematories, etc. However, EPA Region IX (California, Nevada, and Arizona) is second lowest of all EPA regions in the country for estimated total Hg emission from all sources (*21*). Some miscellaneous dispersed sources such as agricultural burning, fungicide application, and dust entrainment were not considered in these inventories but are less likely to be significant.

It is possible that airflow patterns over Tahoe, as described previously, could also entrain Hg volatilized from the waste of historical mining. A tremendous amount of elemental Hg was consumed during the late 1800s at several mining districts regionally close to the Tahoe Basin. Somewhat surprisingly, these historical emissions from the western Sierra Foothills and from Virginia City in Nevada did not produce an unequivocal signal in Lake Tahoe sediments. While elevated concentrations of Hg are found at depth in the west lake core, they do not appear in the south lake core and are significantly modulated in the north lake core. We suggest that high mass sedimentation rates from Comstock logging in the late 1800s diluted most of this historical Hg signal in the two mid-lake cores (*53*). We also note that if Hg volatilized during ore extraction and amalgam processing had been constrained regionally to lower air masses and subject to cold condensation, its subsequent transport over the Sierra Nevada with prevailing winds would have produced a depositional pattern similar to isohyetal contours for the basin—with a greater flux to the west shore and diminishing flux eastward. Since high mass sedimentation rates during Comstock logging of the late 1800s also introduced uncertainty in sediment dating for that period, we have focused on the flux ratio to compare the difference between baseline preindustrial Hg accumulation rates (prior to logging or mining) and the modern rate of accumulation (since 1980). We consider the estimates of Hg deposition reliable for each of these two intervals.

Much of the Hg lost to mining spoils or deposited locally during the mining era would continue to volatilize from depositional surfaces and may gradually be transported downwind across the landscape. Nriagu (*30*) suggested this process, and described it as a grasshopper-type dispersal pattern. He observed that re-emission of only 0.2% of Hg lost during the historical mining era in the Sierras would be equivalent to a substantial fraction of current annual anthropogenic emissions in the United States. This continuous volatilization of Hg^0 from mining spoils and abandoned Hg mines in the Coastal Range, in conjunction with orographic precipitation, scavenging, and cold-condensation, may be contributing to the relatively high rate of modern atmospheric Hg deposition at Lake Tahoe.

One could speculate that Tahoe basin soils were slowly enriched with Hg by this process of atmospheric dispersal since the mining period, and that urbanization in the Tahoe Basin has suddenly moved that Hg-ladened soil to the lake. However, these soils were also enriched in Pb from gasoline combustion, and the sediment concentration profiles for Pb have now stabilized or decreased, while Hg profiles continue to increase. Moreover, stream sediment samples from Tahoe tributaries are slightly enriched in Pb as compared to bedrock but not in Hg (*53*, *76*). Therefore, unless volatilization rates or scavenging efficiency have increased over time, these profiles seem to reflect an increasing rate of Hg input from anthropogenic sources. We cannot say yet whether that Hg input derives predominately from regional, perhaps historical, sources on the west coast or from globally distributed atmospheric Hg, but the regional sources are suspect for up to 85% of THg deposition.

It is relevant to note, however; that one distant source may ultimately impact the west coast. Increased coal combustion in mainland China now produces annual emissions of Hg that are now up to 6-fold greater than U.S. emissions (*77*). High precipitation rates and efficient orographic scavenging could further enhance the deposition of this Hg over the Sierra Nevada. Obviously, a series of sediment sampling transects or deposition monitoring stations are needed across both elevational and latitudinal gradients in the western United States to clarify the relative importance of these sources and processes.

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